

MODIFIED UREA ROUTE(MUR) SYNTHESIS OF Nd^{3+} :

Y_2O_3 NANOPARTICLES SUITABLE FOR

INDUSTRIAL PRODUCTION

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ABSTRACT

Y_2O_3 nanoparticles doped with trivalent Nd^{3+} ($\text{Nd}^{3+}:\text{Y}_2\text{O}_3$) have been synthesized employing a MUR scheme. The characterization included analyses of the results obtained from X-Ray Diffraction, Morphology, size analysis and luminescent emission studies. The results confirmed the presence of yttrium oxide along with the respective dopant (Nd) which was crystalline in nature and of a nano-size between 25nm – 150nm, upon comparison and verification of the characterization results with the reported data. The adopted method has been prudent and apt and can be employed for large scale industrial production for applications in biosensing and imaging. The emission peaks recorded due to the trivalent dopants for a concentration of the dopant (Nd X=10% - 30%) between 896-1356 nm when excited at 808 nm.

KEYWORDS: Rare Earth (RE), ($\text{Nd}^{3+}:\text{Y}_2\text{O}_3$) Nanoparticles (NPs), Modified Urea Route(MUR), Biosensing & Imaging

Received: Jan 08, 2019; **Accepted:** Jan 28, 2019; **Published:** Feb 14, 2019; **Paper Id.:** IJMPERDFEB201962

1. INTRODUCTION

The role that RE ions play in the synthesis and fabrication of smart optical nano-materials has been exemplary due to their longer life time, prominent lines of absorption, outstanding oscillator strength, apart from displaying coherence. This has been possible largely due to the enhancement of the performance when the interaction between the host and the RE ions take place. Though the subject has been consistently pursued by researchers over the last few decades still there is a lot that has to be fathomed regarding the electronic structural relations, energy levels and their electronic states.

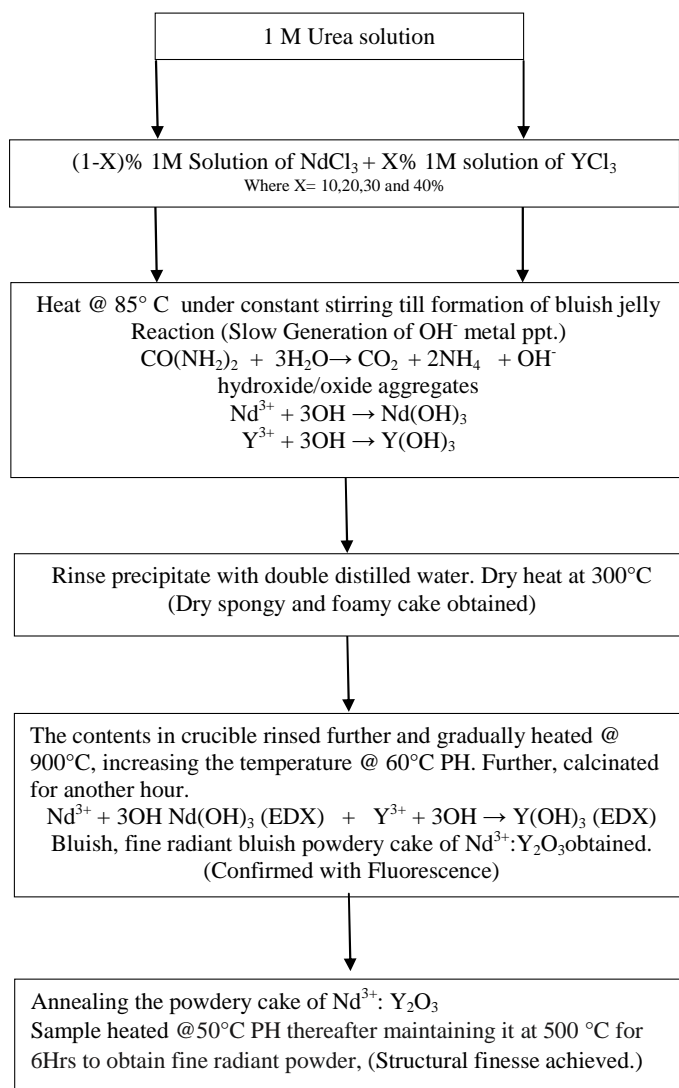
The advent of precision equipment to study the aforesaid properties also enthused the researchers to explore newer applications in technology. Prominent among them have been techniques utilizing Photoconductivity, PL-Excitation, Electron-PE, excited-state absorption and further employing dynamic interactions between different states of energy by controlled excitation [2-11].

These characteristics led into exploring the bio-medical applications of the Nd^{3+} doped Y_2O_3 nanoparticles (NPs) as they were reported to possess non-destructive, non-invasive properties which allows the pathologists to use them for real-time detection of ailments in the human body [12].

This article reports Nd^{3+} as a do pant for the synthesis of NPs due to their prominent absorption and emission characteristics in the wavelength range between 890nm -1400nm. Modified Urea-Route (MUR) method of preparation has been adopted to obtain the $\text{Nd}^{3+}:\text{Y}_2\text{O}_3$ NPs.

2. SYNTHESIS

Different concentrations ($X = 10\% - 40\%$) of 1 M NdCl_3 has been doped into $((100-X)\%)$ concentration of 1 M YCl_3 during the preparation in ethanol along with 1 M urea solution in double distilled water adopting MUR technique [13]. The whole procedure has been depicted using a flowchart for ease of future adoptability.

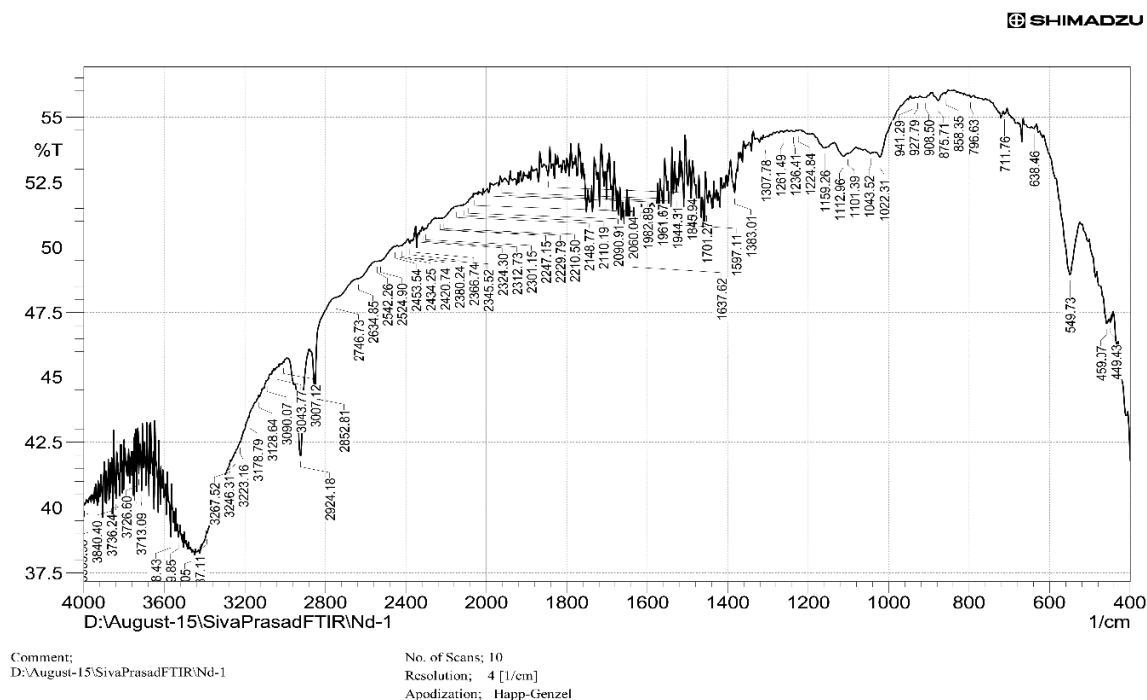


The diffracted rays from the collimated, monochromatic X-rays focused on the fine bluish powder of $\text{Nd}^{3+}:\text{Y}_2\text{O}_3$ satisfying the Bragg condition ($n\lambda = 2d \sin \theta$) confirmed their crystalline nature and nano-size that was in agreement with JCPDS data. Their identity was verified using Fourier Transform IR spectrum and morphology using SEM.

3. RESULTS AND DISCUSSIONS

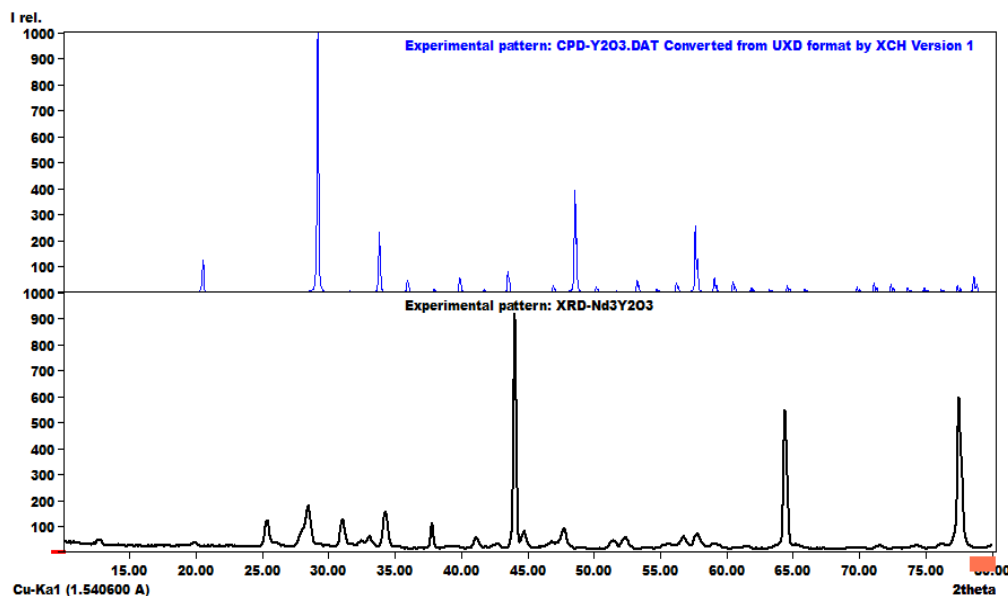
3.1. FTIR Spectroscopy

To identify the functional groups the molecular triggering spectra through FTIR has been recorded. In the Figure 1, Y-O stretching of yttrium oxide occurred at (549.73 cm^{-1}) for the neodymium dopant. [14, 15]. The strong bands of OH-Functional group due to the hygroscopic nature of the rare earths that were observed initially between $3000 - 3500\text{ cm}^{-1}$ which might have been due to the high surface-to-volume ratio of the NPs [16] were phased out through the modification of the Urea route by additionally annealing the sample.



3.2. XRD Analysis

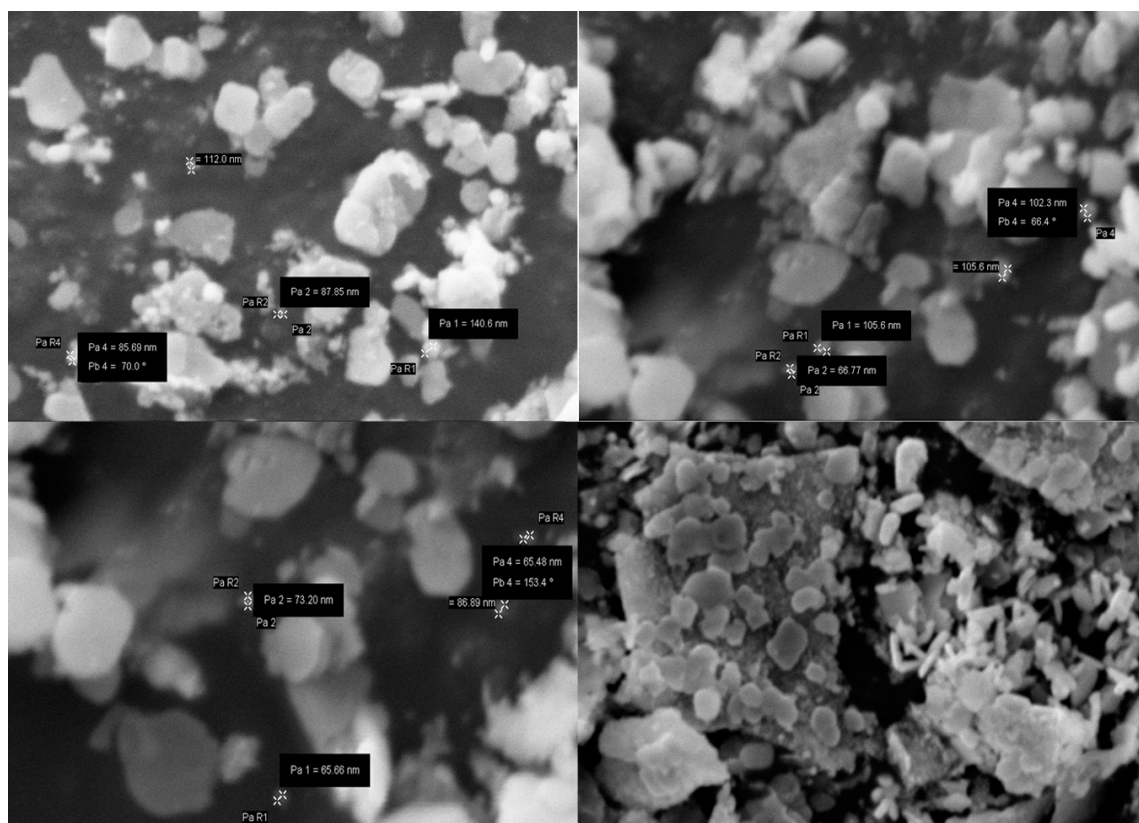
Among the rare earths mostly prominent for doping (*viz.*, Nd, Eu, Gd, Ho, Sm, Yb) neodymium has the largest ionic radius. The amorphous nature of the sample has been observed from the results obtained through the incident Cu k_{α} ($\lambda = 1.5405 \text{ \AA}$) rays on to the precursor gel necessitating the sample to be calcinated, but post calcination only the most prominent of the standard peaks (2 2 2), (4 4 0) and (6 2 2) were observable. Subject to the modification of the urea route procedure [17-18] and annealing the sample further did the trick of enhancing the structure of the $\text{Nd}^{3+}:\text{Y}_2\text{O}_3$ NPs as portrayed. Annealing resulted in improved crystallinity due to the reduction of the area of the surface between the crystallite and its boundary, also suggesting a decreased porosity by the time the process of annealing was completed (6Hrs.) the narrowing down of the peaks Figure 2{(222), (231), (400), (402), (422), (341), (512), (424), (451), (622), (613), (604), (525), (473)} and enhancement of their intensity and width (published elsewhere by the same authors [19]) has been reported through literature [20-23]. The estimated lattice strain ($\varepsilon = 0.002$ to $\varepsilon = 0.006$) in Table 1 has confirmed that there has been no alteration in the phase of the NPs which thus retained their structure, and it has been ascertained that lattice energy varied due to the strained lattice [24] and the spacing between the crystal planes has been observed to be varying from 1.2 to 3.1 nm [25]

Figure 2: Nd³⁺: Y₂O₃ XRD SpectraTable 1: XRD- Analysis of Neodymium doped Yttrium Oxide Nanoparticles – Nd³⁺:Y₂O₃

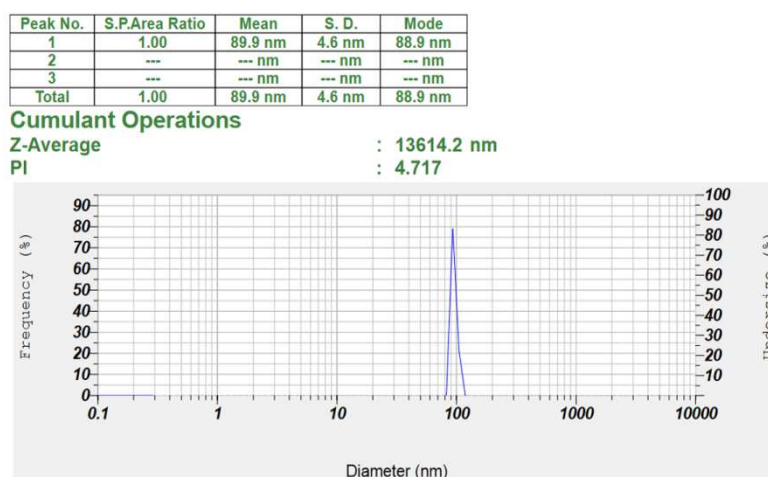
No.	<2Theta>	< FWHM >	$D = \frac{K \lambda}{\beta \cos \theta}$	Lattice Strain ϵ	$\langle d \rangle$ $n\lambda=2d\sin\theta$	HKL Values
1	28.5150	0.4500	19.03	0.0077	3.12774	222
2	31.1167	0.3825	22.53	0.006	2.87190	231
3	33.1322	0.3044	28.45	0.0045	2.70166	400
4	37.8573	0.1904	46.08	0.0024	2.37461	402
5	41.1700	0.3400	26.08	0.004	2.19086	422
6	44.1020	0.1827	49.01	0.0020	2.05177	341
7	47.7862	0.3990	22.75	0.0039	1.90183	512
8	52.2800	0.3680	25.13	0.0033	1.74843	424
9	56.7688	0.3663	25.76	0.003	1.62037	451
10	57.7200	0.2934	32.33	0.0023	1.59591	622
11	57.9000	0.2888	48.88	0.001	1.59138	613
12	64.4667	0.2009	48.83	0.0014	1.44422	604
13	64.7600	0.1346	73.02	0.0009	1.43838	525
14	77.1400	0.1466	75.82	0.0008	1.23550	473

3.3. SEM and Particle Size Analysis

The Nd³⁺: Y₂O₃ NPs were carefully scattered on to a stub and were subjected to low vacuum sputtering ((3x10⁻² mbar) and coated with a metal film (of uniform thickness) to prevent the charging of the sample when exposed to the electron jet. The evolution of gases resulted in porosity of the NPs visible in the images obtained (Figure 3) and have been identified to range in sizes in the range 60 nm – 140 nm. EDAX confirmed the presence of Nd, Y and O proportional to their synthesis concentrations.

Figure 3: $\text{Nd}^{3+}:\text{Y}_2\text{O}_3$ SEM Images

The distribution curve to statistical estimation of the sizes of the NPs has been recorded by analyzing intensity of the light that scattered in a direction perpendicular through the dispersion medium that consisted of the NPs (viscosity – 0.895 mPa.s) at RTP. The NP population has been densely distributed around 90nm size (Figure 4) thus supporting the SEM characterization.

Figure 4: $\text{Nd}^{3+}:\text{Y}_2\text{O}_3$ Particle Size

3.4. Luminescence Studies

The Figure 5 shows the luminescence spectra recorded for different concentrations of the dopant (X = 10%, 20%, 30% and 40%) respectively. The peak analysis has been summarized in the Table 2.

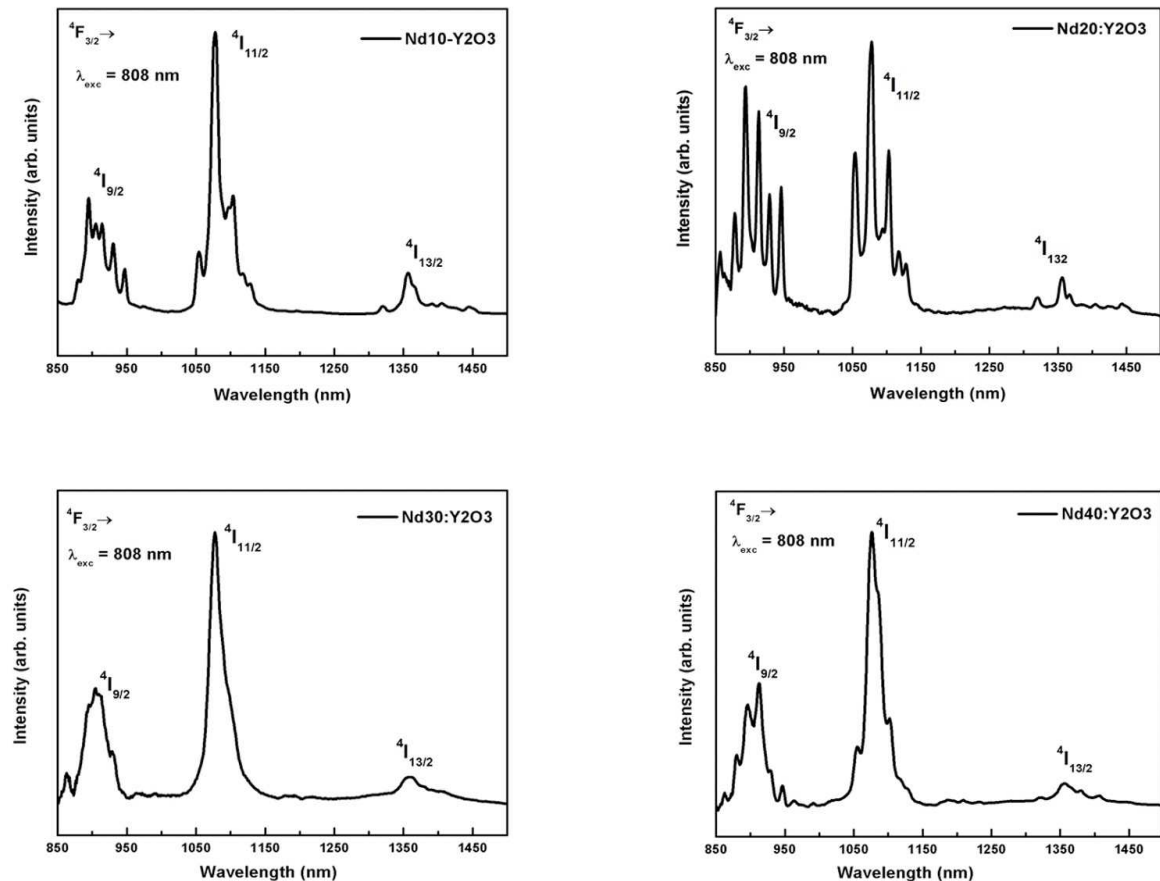


Figure 5: Luminescence Spectra of $\text{Nd}^{3+}:\text{Y}_2\text{O}_3$

Table 2: $\text{Nd}^{3+}:\text{Y}_2\text{O}_3$ Emission Scan (Excited at 808 nm)

Transition States [26]	Range of Wavelength in nm	Identified Peaks in nm
$4F_{3/2} \rightarrow 4I_{9/2}$	896 -912	896, 912
$4F_{3/2} \rightarrow 4I_{11/2}$	1055-1077	1055, 1076
$4F_{3/2} \rightarrow 4I_{13/2}$	1350-1360	1356

The $4F_{3/2} \rightarrow 4I_{11/2}$ near IR Transition holds promise in bio-medical applications due to its non-invasive penetrability into the human tissue. [27]. Further, this aspect could be thoroughly exploited in medical investigations optoacoustic imaging, and as a photosensitizing agent for studying the optical properties of human blood and it has been reported elsewhere [28] that at these wavelengths oxy and deoxy-hemoglobin have isosbestic points for applications in pulse oximeters and oximetry. The strong IR emission allows high pellucidity without resulting in auto-fluorescence that actually had been reported as a emission drawback in UV and visible regions [29].

4. CONCLUSIONS

An economic model that could make the grade for industrial requirements of bulk production has been evolved through the MUR technique. The characterization analysis revealed the capability and applicability of these luminophors in biomedical imaging and diagnostics.

5. MATERIALS AND CHARACTERIZATION INSTRUMENTS

Materials	All the Chemicals used for the synthesis were of AR Grade
Characterization	Details of instrumentation and affiliations with due acknowledgements
UV absorption studies	UV-Vis Spectrophotometer (Jouf University, Qurayat, KSA)
X-ray diffraction (XRD)	XPRT-PRO analytical diffractometer with Cu K α radiation. (Osmania University, Hyderabad, India)
SEM and EDAX	ZEISS SEM Instrument (Osmania University, Hyderabad, India)
FTIR	Shimadzu 8400s instrument (Osmania University, Hyderabad, India)
Particle Size analysis	Horiba SZ-100(Osmania University, Hyderabad, India)
Photoluminescence studies	FLS 980 spectrofluorimeter (Photonics Lab, SV University, Tirupati, India)

6. ACKNOWLEDGEMENTS

The authors wish to thank their employer M/S Jouf University, Saudi Arabia for granting a Major Research Project (No.285/35) where the synthesis of the samples has been carried out at the Nanotechnology Laboratory to pursue this work. The authors wish to thank the Dean, College of Arts and Sciences, Al Qurayat, Jouf University, for providing the required infrastructure to complete the experimental work. The authors thank and duly acknowledge the services provided by the Photonics Lab, SV University, Tirupati, Andhra Pradesh, India and the Nanotechnology Facility at Osmania University, Hyderabad, Telangana, India, where most of the characterization results have been recorded.

REFERENCES

1. C. W. THIEL, Y. SUN, and R. L. CONE, *Journal of Modern Optics* 49, 2399 (2002)
2. Hamilton, D. S., Gayen, S. K., Pogatshnik, G. J., Ghen, R. D., and Miniscalco, W. J., 1989, *Phys. Rev. B*, 39, 8807.
3. Lawson, J. K., and Payne, S. A., 1993, *Phys. Rev. B*, 47, 14003.
4. Mayolet, A., Zhang, W., Simoni, E., Krupa, J. C., and Martin, P., 1995, *Optical Materials*, 4, 757.
5. Pedrini, C., McClure, D. S., and Anderson, C. H., 1979, *J. Chem. Phys.*, 70, 4959.
6. Pedrini, C., Rogemond, F., and McClure, D. S., 1986, *J. Appl. Phys.*, 59, 1196.
7. Raukas, M., Basun, S. A., van Schaik, W., Yen, W. M., and Happek, U., 1996, *Appl. Phys. Lett.*, 69, 3300.
8. Wertheim, G. K., Rosencwaig, A., Cohen, R. L., and Guggenheim, H. J., 1971, *Phys. Rev. Lett.*, 27, 505.
9. Dujardin, C., Pedrini, C., Gâcon, J. C., Petrosyan, A. G., Belsky, A. N., and Vasil'ev, A. N., 1997, *J. Phys.: Condens. Matter*, 9, 5229.
10. Thiel, C. W., Cruguel, H., Wu, H., Sun, Y., Lapeyre, G. J., Cone, R. L., Equall, R. W., and Macfarlane, R. M., 2001, *Phys. Rev. B*, 64, 085107.
11. Blasse, G., Schipper, W., and Hamelink, J. J., 1991, *Inorg. Chim. Acta*, 189, 77.
12. D.K Sardar et al (June 15, 2007). *JAPPL PHYS*, 113115
13. Aghazadeh, M., et al., 2011. *International Scholarly Research Network, ISRN Ceramics*, 2011, pp: 1-6.
14. Guo H, Zhang W, et al., *J Rare Earth* 2004;22:365.
15. S. Pandey, A. et al., *Journal of Display Technology*, vol. 9, no. 12, pp. 989-994, Dec. 2013.
16. Sardar, D. K., K. L. Nash, R.M. Yow, J. B. Gruber, A. Sayka, *Biophotonics International*, Vol. 15, 45-48 (2008).

17. Gagik, G. D., et al, Vol. 105, 063106: 1-7 (2009), *Journal of Applied Physics*.
18. Khalfallah, K. K., Turki, N., & Khelil, M. B. A Fertilizer With Nitrification Inhibitor Dmpp (3, 4-Dimethylpyrazol Phosphate) And Urea As Alternatives To Ammonium Nitrate For Tomato Crop In Tunisia.
19. Aghazadeh, M., Ghaemi, M., Nozad, G. A., Yousefi, T. and Jangju, E. 2011, *International Scholarly Research Network, ISRN Ceramics*, 2011, pp: 1-6.
20. Guo H, Zhang W, Yin M, Lou L, Xia S. *J Rare Earth* 2004;22:365.
21. S. Pandey, A. Pandey and V. K. Rai, *Journal of Display Technology*, vol. 9, no. 12, pp. 989-994, Dec. 2013. doi: 10.1109/JDT.2013.2275964
22. Cullity BD (1957) *Elements of X-ray diffraction*. Am J Phys 25:394–395
23. Hajizadeh-Oghaz, M., Razavi, R.S., Barekat, M. et al. *J Sol-Gel Sci Technol* (2016) 78: 682. doi:10.1007/s10971-016-3986-3
24. Siva Prasad Peddi, Bilal Sadeh, 92, (2015) 012004, *IOP Conf. Series: Materials Science and Engineering*,
25. S P PEDDI, BILAL A S, & Y. A HAYE, Vol. 5, Issue 4, Dec 2015, 1-8, *International Journal of Semiconductor Science & Technology (IJSST)* ISSN(P): 2250-1576; ISSN(E): 2278-9405,
26. Abu-Hashim, M. S. D., Salama, A., & Garbout, A. (2015). *Characterization Of Soil-Root Interactions Using Medical X-Ray Computed Tomography Technique*. *International Journal of Agricultural Science and Research (IJASR)*, 5(5), 159-170.
27. Ghasemi A, Mousavinia M, 40(2):2825–2834, *Ceramics Int*, 2014
28. Vetrone, F., Boyer, J.-C., Capobianco, J.A., Speghini, A. and Bettinelli, M. (2004), *Journal of Materials Research*, 19(11), pp. 3398–3407. doi: 10.1557/JMR.2004.0438.
29. Gaboriaud, R.J.; Jublot, M.; Paumier, F.; Lacroix, B. *Nucl.Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, 2013, 310, 6. DOI: 10.1016/j.nimb.2013.05.014.
30. NJ Shivaramu, BN Lakshminarasappa, KR Nagabhushana, F Singh, VBRI press in 2015 *Interact. with Mater. Atoms*, 2013, 310, 6. DOI: 10.1016/j.nimb.2013.05.014.